

CCSF PHYC 4D Lecture Notes

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Chapter 3

The Particle-like Properties of Electromagnetic Radiation

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Electromagnetic waves

- Electromagnetic waves:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \sin(\vec{k} \cdot \vec{r} - \omega t) \quad \vec{B}(\vec{r}, t) = \vec{B}_0 \sin(\vec{k} \cdot \vec{r} - \omega t) \quad \vec{E}_0 \perp \vec{B}_0 \perp \vec{k}$$

$$k = 2\pi/\lambda \quad \omega = 2\pi\nu \quad B_0 = E_0/c$$

- Intensity is the magnitude of the Poynting vector:

$$I = \left| \frac{1}{\mu_0} \vec{E} \times \vec{B} \right| = \frac{1}{\mu_0 c} E_0^2 \sin^2(\dots) \rightarrow \frac{1}{2\mu_0 c} E_0^2 \quad (\text{time average})$$

Intensity is proportional to amplitude squared (general wave result).

Double-slit experiment

- Setup: waves approach double slit (separation d). Two waves interfere at a distant screen ([Ch3:p1])

- Interference result:

$$\Delta N = \frac{\Delta L}{\lambda} = \frac{d \sin \theta}{\lambda}$$
$$d \sin \theta = (\Delta N) \lambda$$

- Bright fringes:

$$d \sin \theta = m \lambda$$

- Dark fringes:

$$d \sin \theta = (m + \frac{1}{2}) \lambda$$

- Effects of multiple slits, each separated by d . Bright fringes become bright spots with most of the space in between dark. Illustrative example: imagine what happens with 10 slits if $\Delta N = 3.1$ between adjacent slits (0 cancels 5, 1 cancels 6, etc).

Bragg scattering

- Electromagnetic waves scatter off planes of atoms (normally x-rays are used) and are observed on a distant screen ([Ch3:p1]).

- Interference result:

$$\Delta N = \frac{\Delta L}{\lambda} = \frac{2d \sin \theta}{\lambda}$$

$$2d \sin \theta = (\Delta N)\lambda$$

- Bright spots (multiple planes, so analogous to multiple slits):

$$2d \sin \theta = m\lambda$$

Equipartition theorem and its failure

- Quantum mechanics becomes relevant at atomic length scales. First symptoms that classical physics was failing occurred in thermodynamics, which deals with the collective behavior of large numbers of atoms.
- Equipartition theorem (important result of classical thermodynamics): each “mode” carries an average kinetic energy of $\frac{1}{2}kT$. Furthermore, modes which are characterized by harmonic oscillation carry an average potential energy of $\frac{1}{2}kT$ as well.
- What is a mode? One atom: 3 directions of motion = 3 modes.
- Two atoms: (1) 3 directions of motion each = 6 modes; OR (2) 3 directions of cm motion + 2 independent rotations + 1 vibration = 6 modes.
- N atoms: $3N$ modes (3 independent motions for each atom). These modes can also be accounted for by overall cm motion (3), overall rotation (3), and vibrational ($3N - 6$), some low frequency (long range) and some high frequency (short-range).
- In 1859, Maxwell used the equipartition theorem to derive specific heats for ideal gases. His calculations did not agree with experiment.
- Further evidence of the failure of the equipartition theorem is given by the blackbody spectrum, discussed next.

Blackbody radiation

- It had been known well before 1900 that all objects emit electromagnetic radiation. The spectrum can be described by the radiancy, $R(\nu)$, which is defined by the radiation intensity in a given frequency interval $[\nu, \nu + d\nu]$:

$$dI = R(\nu) d\nu$$

The spectrum for a perfect blackbody depends only on the object's temperature.

- For a non-blackbody, the radiancy is reduced by the same factor as the absorption. Example: if an object absorbs only $\frac{2}{3}$ of the incident radiation at a given frequency (reflecting the rest), then it will emit only $\frac{2}{3}$ of what a perfect blackbody would emit. This is a consequence of thermodynamics.
- (Note: dates are unconfirmed; blackbody curves as early as 1862?) In the 1870's and 1880's, the first experimental results were confirmed: the total intensity emitted by a perfect blackbody is proportional to T^4 (Stefan-Boltzmann Law) and the radiancy peaks at a frequency that is proportional to temperature (equivalent to Wien's displacement law, normally expressed in terms of wavelength).

$$I = \sigma T^4 \quad \sigma = 5.670 \times 10^{-8} \text{ W/m}^2/\text{K}^4$$

$$\lambda_{\text{max}} T = 2.898 \times 10^{-3} \text{ m K}$$

- By the early 1890's, the radiancy $R(\nu)$ had been pretty much determined experimentally.
- In 1900, Rayleigh determined the frequency dependence of $R(\nu)$ by applying the equipartition theorem to the modes of electromagnetic radiation in a box. Rayleigh and Jeans later refined this calculation by determining the constants. The result completely defies nature (and reason), giving rise to the so-called "ultraviolet catastrophe".
- In the same year, Planck resolved the dilemma by making an assumption: electromagnetic radiation of a given frequency can only exist in certain quanta whose energy is proportional to frequency: $E = h\nu$ (this

restriction invalidates the equipartition theorem, especially for the high-frequency modes where the Planck restriction is a severe limitation on allowable energy values). He was able to fit the experimental data perfectly. However, it was some time before even he actually accepted the idea that light came in this form.

- Imagine a cubic box at temperature T . Its inner (conducting) walls emit and absorb EM radiation, establishing a spectrum of EM radiation inside the box in thermal equilibrium with the box itself. If we punch a small hole in the box, that hole will radiate as a (nearly) perfect blackbody. The radiancy can be related to the energy density of the radiation inside the box:

$$R(\nu) d\nu = \frac{1}{4}cu(\nu) d\nu$$

(This is analogous to $\vec{J} = \rho\vec{v}$ for charges or mass — the factor of $\frac{1}{4}$ is due to the fact that not all radiation travels in the same direction.)

- Counting standing wave modes in the $a \times a \times a$ cubic box:
 - 1-D standing wave (e.g., on a string):

$$y(x, t) = A \sin(kx) \sin(\omega t)$$

- If y vanishes at the boundary, then

$$ka = \pi n \quad \omega = ck = \frac{\pi c}{a}n$$

- Define $\Lambda(\omega)$ to be the number of modes (i.e., possible values of n or k) such that $\omega_n = (\pi c/a)n \leq \omega$. This condition is equivalent to $n \leq a\omega/(\pi c)$, and so

$$\Lambda(\omega) = \frac{a\omega}{\pi c}$$

- Define $N(\omega) d\omega$ to be the number of modes between ω and $\omega + d\omega$.

$$N(\omega) d\omega = \Lambda(\omega + d\omega) - \Lambda(\omega) = \frac{d\Lambda}{d\omega} d\omega = \frac{a}{\pi c} d\omega$$

- 3-D standing wave:

$$Y(\vec{r}, t) = A \sin(k_x x) \sin(k_y y) \sin(k_z z) \sin(\omega t)$$

If Y vanishes at the boundary then

$$\vec{k} = \frac{\pi}{a}(n_x \hat{x} + n_y \hat{y} + n_z \hat{z}) = \frac{\pi}{a} \vec{n}$$

– $\omega_{\vec{n}} \leq \omega$ is equivalent to $|\vec{n}| \leq a\omega/(\pi c)$, so

$$\Lambda(\omega) = \frac{1}{8} \frac{4}{3} \pi \left(\frac{a\omega}{\pi c} \right)^3 = \frac{V}{6\pi^2 c^3} \omega^3$$

$$N(\omega) d\omega = \frac{d\Lambda}{d\omega} d\omega = \frac{V}{2\pi^2 c^3} \omega^2 d\omega$$

– Express in terms of ν ($\nu = \omega/2\pi$, $d\nu = d\omega/2\pi$):

$$N(\nu) d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

– For electromagnetic radiation in a box, there are two polarizations, so

$$N(\nu) d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu$$

- Rayleigh-Jeans combined this result with the equipartition theorem: every such mode carried with it an average energy of kT , so

$$U(\nu) d\nu = (N(\nu) d\nu) kT$$

and so,

$$R(\nu) = \frac{1}{4} c \frac{U(\nu)}{V} = \frac{2\pi \nu^2 kT}{c^2}$$

Total intensity

$$I = \int_0^\infty R(\nu) d\nu = \infty$$

The divergence is due to high frequencies.

- The reason why the average energy per mode is kT and not $\frac{1}{2}kT$ for electromagnetic radiation has to do with the relationship between kinetic energy and momentum: $K = pc$ for photons, whereas $K = p^2/2m$ for non-relativistic particles.
- Planck assumed that electromagnetic radiation is quantized, with an energy quanta proportional to frequency ($E = h\nu$). This invalidates the classical equipartition theorem, resulting in an average energy per mode of $h\nu/(e^{h\nu/kT} - 1)$. He derived his blackbody radiation formula

$$R(\nu) = \frac{2\pi h \nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

which fit the data perfectly. Subsequent refinements of experimental data fit his formula even better (always a good sign).

- At low frequency ($h\nu \ll kT$), the quantization assumption is consistent with the continuity assumption that leads to the equipartition theorem, and the Planck formula reduces to the Rayleigh-Jeans formula [demonstrate].
- At high frequency ($h\nu \gg kT$), the equipartition theorem is severely compromised — with such a high energy barrier to creating even a single quanta, it is unlikely that the total energy in the mode will be different from zero. The average energy in the mode will be *much* less than kT . This shuts down the radiancy at high frequency and solves the ultraviolet catastrophe.
- Example: $h\nu = 10kT$ implies that

$$\frac{h\nu}{e^{h\nu/kT} - 1} = \frac{10kT}{e^{10} - 1} \approx \frac{10kT}{22000} \approx (5 \times 10^{-4})kT$$

Energy per mode for $h\nu = 20kT$ is down to about $(4 \times 10^{-8})kT$.

- Q3-15[Q3-16]: Wien’s displacement theorem. Q3-16[Q3-17]: Stefan-Boltzmann Law.
- It turns out that the quantum harmonic oscillator has the same set of allowable energies ($E = nh\nu$) as electromagnetic radiation. Thus, the same type of quantization argument also resolves the specific heat problem encountered by Maxwell. High frequency vibrational modes tend to be “frozen out” at low temperatures ($h\nu \gg kT$) — those modes do not contribute to the specific heat of the object (as Maxwell had assumed that they did). When the temperature increases to on the order of $h\nu/k$, those modes “turn on” and start contributing to the specific heat. A plot of specific heat vs. temperature tends to resemble a step-like function.
- Note: The definitions of terms such as radiancy seem to be in some controversy. Several related quantities:
 - power per area (intensity)
 - intensity per unit frequency (or wavelength) interval
 - intensity per unit solid angle

- intensity per unit frequency (or wavelength) interval per unit solid angle

All of these are named with combinations of the words “(ir-)radiance / radiant / radiancy”, “spectral”, “energy”, “power”, and “intensity”. According to wikipedia, what we (and our textbook) have called radiancy is actually supposed to be called “spectral irradiance”. Go figure. . .

Photoelectric Effect

- When electromagnetic radiation is incident upon a metal surface, electrons are emitted. Discovered by Hertz (also discovered EM radiation) in 1887. Several experimental characteristics were well known by 1902.
- Experimental setup (Fig. 3.9[3.10] on p. 76[72]) (Ch3:p2). EM radiation is incident upon emitter. Electrons are emitted and some of them reach the collector.
- Rate of electron charge transfer to the collector (photocurrent) can be measured by the ammeter (4DL experiment: photocurrent is likely to be pA).
- Energy supplied by EM radiation to a single electron (E_{EM}) must first be used to ionize the electron (Φ — workfunction); the remainder is converted to kinetic energy (K)

$$E_{\text{EM}} = \Phi + K$$

Φ depends on material and is normally a few eV.

- Maximum kinetic energy (K_{max}) can be measured by applying an external potential and increasing it until the photocurrent reaches zero (stopping potential V_{stop}).

$$K_{\text{max}} = eV_{\text{stop}}$$

In the 4DL photoelectric effect experiment, you will measure V_{stop} directly with a voltmeter (this requires a very high impedance voltmeter since the photocurrent is so low).

- Classical predictions:
 - K_{\max} increases with increasing intensity (E_{EM} increases because electric field is higher). Below intensity cutoff, no electrons are emitted. (Ch3:p3) (or does it take longer to emit them?)
 - Frequency should not make any difference.
 - First electrons should be emitted after about 1 s (depends on intensity).
- Experimental results:
 - K_{\max} is independent of the intensity. When $V_{\text{ext}} < V_{\text{stop}}$, the photocurrent increases with intensity, but that current drops to zero at the same stopping potential no matter what the intensity is (Fig. 3.10[3.11] on p. 77[74]).
 - K_{\max} depends linearly on frequency of the radiation (Ch3:p3). Below a certain cutoff frequency, no electrons are observed at all.
 - The first photoelectrons appear within 1 ns of the incident EM radiation.
- Einstein's model:
 - EM radiation comes in discrete particles whose energy depends linearly on frequency (Planck's hypothesis).

$$E = h\nu$$

- Electron is released when it interacts with a *single* photon.

$$E_{\text{EM}} = h\nu = \Phi + K_{\max}$$

- If $\nu < \nu_{\text{cutoff}} = \Phi/h$, no electrons are emitted.
- If $\nu \geq \nu_{\text{cutoff}}$, electrons are emitted with a maximum kinetic energy

$$K_{\max} = eV_{\text{stop}} = h\nu - \Phi$$

This depends linearly on ν .

- Intensity affects the *rate* of photon incidence, and therefore affects the photocurrent when electrons are emitted, but it does not affect the energy of each photon, and hence K_{\max} is unchanged, as is the cutoff frequency.

- Plot of V_{stop} vs. ν should be a straight line with slope h/e . Millikan measured this ratio in 1915 and obtained a value for h which was consistent with Planck's blackbody spectrum (e was measured earlier by Millikan in 1910–1913).

Compton Effect

- Photons incident upon a metal surface with an energy of a few eV are likely to be absorbed completely by an electron as the electron is ejected from the material, as described by the photoelectric effect.
- Photons of much higher energies are more likely to *scatter* off of an electron, freeing it, with a new photon reemitted. Photons can also scatter off of the entire atom if the electron is not freed. This effect was discovered by Compton in 1923.
- Photon scatters off a stationary mass m (Ch3:p4). Angle of photon scattering is ϕ .
- Energy-momentum conservation:

$$\mathbf{p}_{\gamma i} + \mathbf{p}_{mi} = \mathbf{p}_{\gamma f} + \mathbf{p}_{mf}$$

$$\mathbf{p}_{\gamma i} = (E_{\gamma i}, \vec{p}_{\gamma i}) \quad \mathbf{p}_{mi} = (m, \vec{0}) \quad \mathbf{p}_{\gamma f} = (E_{\gamma f}, \vec{p}_{\gamma f})$$

$$\begin{aligned} m^2 &= \mathbf{p}_{mf}^2 = (\mathbf{p}_{mi} + \mathbf{p}_{\gamma i} - \mathbf{p}_{\gamma f})^2 \\ &= m^2 + 0 + 0 + 2\mathbf{p}_{mi} \cdot \mathbf{p}_{\gamma i} - 2\mathbf{p}_{mi} \cdot \mathbf{p}_{\gamma f} - 2\mathbf{p}_{\gamma i} \cdot \mathbf{p}_{\gamma f} \\ &= m^2 + 2mE_{\gamma i} - 2mE_{\gamma f} - 2(E_{\gamma i}E_{\gamma f} - \vec{p}_{\gamma i} \cdot \vec{p}_{\gamma f}) \end{aligned}$$

$$m(E_{\gamma i} - E_{\gamma f}) = E_{\gamma i}E_{\gamma f}(1 - \cos \phi)$$

$$1/E_{\gamma f} - 1/E_{\gamma i} = (1/mc^2)(1 - \cos \phi)$$

Since $E_{\gamma} = h\nu = hc/\lambda$,

$$\lambda_f - \lambda_i = \frac{h}{mc}(1 - \cos \phi)$$

- Classical prediction is that $\nu_f = \nu_i$. Quantity h/mc is the Compton wavelength of particle of mass m .

- If the electron is ejected from the atom, then m is equal to the electron mass.

$$h/m_e c = hc/m_e c^2 = 1240 \text{ MeV fm} / 0.511 \text{ MeV} = 2.43 \text{ pm}$$

- If the electron is not removed from the atom, the photon scatters off of the entire atom. In that case, m is the mass of the atom. The Compton wavelength of the proton is given by

$$h/m_p c = hc/m_p c^2 = 1240 \text{ MeV fm} / 938 \text{ MeV} = 1.32 \text{ fm}$$

- Compton's data is shown in Fig 3.20–22 (p. 90[87]). Double peak includes scattering events where the electron is and is not freed. (Spread of peaks may be due to Doppler effect.)

Bremsstrahlung / X-ray production

- When a moving beam of electrons encounter atoms, they will interact and slow down. Accelerating electrons emit electromagnetic radiation in the form of photons. Energy conservation requires

$$h\nu = -\Delta K$$

- In general, several photons may be emitted by a given electron as it accelerates to rest. This can give rise to a continuum of photon energies.
- If electrons are accelerated through a potential difference V from rest, they will have an initial kinetic energy $K_i = eV$. Maximum frequency given by

$$\nu_{\max} = |\Delta K|_{\max}/h = (K_i - 0)/h = eV/h$$

$$\lambda_{\min} = c/\nu_{\max} = hc/eV$$

For $V = 10 \text{ kV}$ (typical), $\lambda_{\min} = 0.124 \text{ nm}$ (x-rays).

- For $V = 500 \text{ V}$ (CRT experiment, 4BL), $\lambda_{\min} = 1240 \text{ eV nm} / 500 \text{ V} = 2.5 \text{ nm}$ (far UV, soft X-ray). Relatively safe.
- Experimental results given in Fig. 3.24 (p. 93[89]).

- $e^- \rightarrow e^- + \gamma$ cannot conserve energy in the rest frame of the original electron. Photon will not be emitted unless the electron interacts with something else (e.g., an atom).

Pair production / annihilation

- A photon can be converted into two anti-particles; e.g., an electron (e^-) and a positron (e^+).
- Photon energy must be at least the sum of the rest energies of the two particles:

$$E_\gamma = m_{e^-}c^2 + K_{e^-} + m_{e^+}c^2 + K_{e^+} \geq 2m_e c^2$$

Any photon energy beyond $2m_e c^2$ is converted into kinetic energy of the electrons (+ whatever the photon collides with; see next point).

- Pair production requires another particle (e.g., an atom) to act as a repository for momentum.

$$\gamma \rightarrow e^- + e^+$$

cannot happen on its own, because it cannot happen in a reference frame where $E_\gamma < 2m_e c^2$. Without the presence of the atom to establish a reference frame, one can always choose a reference frame where the photon has been red-shifted to arbitrarily low energy.

- The reverse process where two anti-particles collide and annihilate is also possible. The result is two or more photons.
- Conversion to a single photon

$$e^- + e^+ \rightarrow \gamma$$

would be the inverse of the pair production interaction, which cannot happen on its own. Alternative argument: in the “center-of-momentum” frame of the two anti-particles, the outgoing photon would have to have zero momentum, and hence zero energy.

Particle vs. wave

- Is electromagnetic radiation a particle or wave? It is both.
- EM radiation acts as a particle during (1) emission (creation), (2) absorption (destruction), and (3) interaction with something else.
- EM radiation acts as a wave during propagation.
- The same EM radiation will act both as a wave and as a particle, hence the two properties cannot be regarded in any way as mutually exclusive.
- Example: Consider a double slit experiment with a phototube in front of the screen (Ch3:p5). When EM radiation is incident upon the phototube, it acts as a particle, (possibly) ejecting electrons towards the collector at a certain rate (measured by the ammeter). That rate depends on the intensity of the EM radiation at the position where the phototube is located. The interference pattern will be evident in the experimental results, which demonstrates that the same EM radiation acted as a wave as it passed through the double slit. If the source is a blackbody at a certain temperature, the EM radiation spectrum will match the Planck spectrum, demonstrating that the radiation acts as a particle during emission. Other types of emission processes also involve the particle nature of EM radiation.
- In the 4DL photoelectric effect experiment, an atomic light source emits EM radiation at specific frequencies, which are related to the energy levels of the emitting atoms and the relationship between photon energy and frequency (EM radiation acts as a particle at emission). That same radiation is then split into the different frequencies with a diffraction grating (EM radiation acts as a wave when passing through the grating). That EM radiation is then incident upon the emitter of the phototube, allowing you to demonstrate the particle nature of EM radiation at absorption.
- It will turn out that electrons, and other “particle-waves” behave exactly the same way; the subject of Chapter 4...

Appendix: Statistical Mechanics

- In this appendix, we introduce some concepts from statistical mechanics, and then calculate the average energy per mode in various circumstances. We derive the equipartition theorem based on classical mechanics, and then show the modifications which occur when quantum behavior is taken into account. This will not be covered in class.
- Statistical mechanics is the study of the macroscopic behavior of large systems of particles. The behavior of such large systems is largely governed by statistical averages.
- The average (or expected) value of a given quantity “ q ” is given by

$$\langle q \rangle = \sum_n q_n P_n$$

where the sum is over all possible “states” of the system, q_n is the value of q for state n and P_n is the probability that the system is in state n .

- If the system is in thermodynamic equilibrium with a temperature of T , then the probability of occupying a given state is proportional to the so-called *Boltzmann factor* $e^{-E_n/kT}$, where E_n is the energy associated with state n . More precisely, the probabilities are given by

$$P_n = \frac{e^{-E_n/kT}}{Z} \quad Z = \sum_n e^{-E_n/kT}$$

The normalization factor Z is called the *partition function* of the system. Putting all of this together yields

$$\langle q \rangle = \frac{\sum_n q_n e^{-E_n/kT}}{\sum_n e^{-E_n/kT}}$$

- In classical physics, a state is determined by specifying a point in *phase space*, which involves specifying the positions (\vec{r}_i) and momenta (\vec{p}_i) of all particles. For a system of N particles ($3N$ modes), a total of $6N$ coordinate values must be specified ($3N$ position coordinates and $3N$ momentum coordinates).

- For a single particle moving in one dimension (hardly a “large” system), a point in phase space is given by (x, p) . The expectation value of q is given by

$$\langle q \rangle = \frac{\iint q(x, p) e^{-E(x, p)/kT} dx dp/h}{\iint e^{-E(x, p)/kT} dx dp/h}$$

- The states are assumed to be distributed with uniform density in phase space: $dx dp/h$ is the number of states in the region of phase space $[x, x + dx] \times [p, p + dp]$. The constant h has the same units as Planck’s constant, and may be assumed to be Planck’s constant itself. This is an interesting development, since the theory we are describing is a classical theory. In any case, the value of h makes no difference since it cancels out of the numerator and denominator.
- In general, energy can be divided into kinetic and potential energy:

$$E(x, p) = K(p) + U(x)$$

The average value of kinetic energy can be computed as follows:

$$\begin{aligned} \langle K \rangle &= \frac{\iint K(p) e^{-E(x, p)/kT} dx dp}{\iint e^{-E(x, p)/kT} dx dp} \\ &= \frac{\left(\int K(p) e^{-K(p)/kT} dp \right) \left(\int e^{-U(x)/kT} dx \right)}{\left(\int e^{-K(p)/kT} dp \right) \left(\int e^{-U(x)/kT} dx \right)} \\ &= \frac{\int_0^\infty K(p) e^{-K(p)/kT} dp}{\int_0^\infty e^{-K(p)/kT} dp} \\ &= S_1/S_0 \end{aligned}$$

where S_1 and S_0 are, by definition, the numerator and denominator. Note that the original integrals over phase space factor because kinetic energy only depends on p and $e^{-(K+U)/kT} = e^{-K/kT} e^{-U/kT}$. The position integrals involving $U(x)$ cancel out. The momentum integrals should be taken over the range $[-\infty, +\infty]$, but can alternatively be taken over $[0, \infty]$ because $K(-p) = K(p)$ and the factors of 2 will cancel.

- One of the best ways of doing an integral is to somehow *avoid* doing the integral. If we apply integration by parts to S_0 ($u = e^{-K(p)/kT}$, $du = (-K'(p)/kT) e^{-K(p)/kT} dp$, $v = p$, $dv = dp$) we obtain:

$$S_0 = \int_0^\infty e^{-K(p)/kT} dp$$

$$= pe^{-K(p)/kT} \Big|_0^\infty + (1/kT) \int_0^\infty pK'(p)e^{-K(p)/kT} dp$$

If $K(p) = Cp^n$, then $pK'(p) = nK(p)$ and the result reduces to $S_0 = (n/kT)S_1$, and so

$$\langle K \rangle = \frac{S_1}{S_0} = \frac{1}{n}kT$$

- In the non-relativistic regime, $K(p) = p^2/(2m)$, $n = 2$, and so the average kinetic energy for this single-mode system is $\frac{1}{2}kT$, as stated by the equipartition theorem. This is appropriate when $kT \ll mc^2$.
- In the extreme relativistic regime, $K(p) = |p|c$, $n = 1$, and so the average kinetic energy is kT . This is appropriate for electromagnetic radiation, as well as other situations where $kT \gg mc^2$.
- In the intermediate range, $K(p) = \sqrt{p^2c^2 + m^2c^4} - mc^2$, and the integrals become very complicated. In this case, the average kinetic energy lies somewhere between $\frac{1}{2}kT$ and kT , depending on the exact value of kT/mc^2 .
- Technical note: The last sentence above has been verified with the help of a graphing program that can evaluate integrals numerically. A more robust verification is pending. It can be shown that:

$$\langle K \rangle = kT \frac{\int_0^\infty f(x)e^{-f(x)} dx}{\int_0^\infty e^{-f(x)} dx}$$

where

$$f(x) = \sqrt{x^2 + \alpha^2} - \alpha \quad \alpha = mc^2/kT$$

It is easily shown that

$$x \geq \sqrt{C^2 + 2\alpha C} \Rightarrow f(x) \geq C$$

which can be used to help determine an appropriate upper limit on the integrals (numerical integration out to infinity isn't exactly feasible).

- Average potential energy can be treated the same way. If the particle is a free-particle, then $U = 0$, and clearly $\langle U \rangle = 0$. If the particle is a

harmonic oscillator ($U(x) = \frac{1}{2}Cx^2$), then

$$\begin{aligned}
\langle U \rangle &= \frac{\iint U(x) e^{-E(x,p)/kT} dx dp}{\iint e^{-E(x,p)/kT} dx dp} \\
&= \frac{\left(\int e^{-K(p)/kT} dp \right) \left(\int U(x) e^{-U(x)/kT} dx \right)}{\left(\int e^{-K(p)/kT} dp \right) \left(\int e^{-U(x)/kT} dx \right)} \\
&= \frac{\int_{-\infty}^{\infty} U(x) e^{-U(x)/kT} dx}{\int_{-\infty}^{\infty} e^{-U(x)/kT} dx} \\
&= \frac{1}{2}kT
\end{aligned}$$

The phase space integrals factor in exactly the same way as they did for the kinetic energy, and the end result is exactly the same as for the quadratic kinetic energy function $K(p) = p^2/(2m)$. Evidently, a non-relativistic harmonic oscillator has an expected total energy of kT , $\frac{1}{2}kT$ of kinetic energy, and $\frac{1}{2}kT$ of potential energy.

- For a system of N particles ($3N$ modes), the phase space integrals consist of integrals over all $3N$ position and $3N$ momentum coordinates. When computing $\langle K \rangle$ and $\langle U \rangle$ associated with each individual mode, the phase space integrals factor, and all but one of them cancel out. The result is an average kinetic energy of $\frac{1}{2}kT$ or kT (or somewhere in between) for each mode, and an additional average potential energy of $\frac{1}{2}kT$ for each vibrational mode.
- The equipartition theorem makes essential use of classical physics, in that it is assumed that all possible values of x and p (and hence energy) are allowed. In quantum mechanics, energy takes on discrete values. This can have a profound impact on the average energy calculation.
- Let's focus on a single mode (i.e., single possible standing-wave pattern) of electromagnetic radiation in a box. According to the Planck hypothesis, this radiation consists of an integer number of photons, each with energy $h\nu$. The state of this quantum system is determined by specifying the number of photons n . The energy of state n is given by $E_n = nE_0 = nh\nu$.
- The average energy can now be computed by direct summation:

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nE_0 e^{-nE_0/kT}}{\sum_{n=0}^{\infty} e^{-nE_0/kT}}$$

$$\begin{aligned}
&= \frac{E_0 \sum_{n=0}^{\infty} n r^n}{\sum_{n=0}^{\infty} r^n} \\
&= \frac{E_0 S_1}{S_0}
\end{aligned}$$

where $r = e^{-E_0/kT} < 1$ and S_1 and S_0 are the sums in the numerator and denominator, respectively. The sum S_0 is a geometric series.

- The sums can be evaluated as follows:

$$\begin{aligned}
S_1 &= \sum_{n=0}^{\infty} n r^n \\
&= \sum_{n=0}^{\infty} (n+1) r^{n+1} \quad (\text{re-index}) \\
&= r \left(\sum_{n=0}^{\infty} n r^n + \sum_{n=0}^{\infty} r^n \right) \\
&= r(S_1 + S_0)
\end{aligned}$$

Rearranging yields

$$S_1 = \frac{r S_0}{1 - r} = \frac{S_0}{1/r - 1}$$

and so

$$\langle E \rangle = \frac{E_0 S_1}{S_0} = \frac{E_0}{e^{E_0/kT} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

- For low frequencies ($h\nu \ll kT$), this reduces to the classical result (kT for EM radiation). For high frequencies ($h\nu \gg kT$) where the quantization condition is severely limiting, the average energy decreases exponentially to zero. Combining this result with the number of modes $N(\nu) d\nu$ yields the Planck blackbody spectrum.
- It turns out that a single mode quantum harmonic oscillator has the same energy spectrum

$$E_n = n h \nu$$

where ν is the classical vibrational frequency of the mode. This will be shown in Chapter 5. The average total energy of this vibrational mode is given by

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT} - 1}$$

using *exactly* the same calculation as the photon calculation above. Again, for $h\nu \ll kT$, this reduces to the classical result kT ($\frac{1}{2}kT$ kinetic plus $\frac{1}{2}kT$ potential), but for $h\nu \gg kT$, the average total energy of this vibrational mode is practically zero.

- A proper calculation of the specific heats of ideal gases must take the quantum behavior of the vibrational modes into account. A diatomic atom consists of six modes: three translational, two rotational, and one vibrational mode. The translational and rotational modes can generally be treated classically, and each contribute $\frac{1}{2}kT$ of kinetic energy, for a total of $\frac{5}{2}kT$ per molecule.

- At sufficiently high temperatures ($kT \gg h\nu$), the vibrational mode contributes kT , for a total of $\frac{7}{2}kT$ per molecule. The specific heat is given by

$$c_v = \frac{1}{N} \frac{dE}{dT} = \frac{1}{N} \frac{d}{dT} \left(\frac{7}{2} N k T \right) = \frac{7}{2} k$$

- At low temperatures ($kT \ll h\nu$), the vibrational mode will “freeze out” (contribute practically zero energy), thus giving a specific heat of $\frac{5}{2}k$.
- For intermediate temperatures ($kT \sim h\nu$), the contribution from the vibrational mode is more complicated, and the resulting specific heat lies somewhere between $\frac{5}{2}k$ and $\frac{7}{2}k$. The plot of c_v vs. T resembles a step-function curve. Note that the transition temperature depends on the frequency of the vibrational mode, and is different for different diatomic molecules. Maxwell was unaware of this quantum behavior of the vibrational modes and made the wrong prediction.
- At extremely low temperatures, the quantum behavior of the rotational and translational motions must also be taken into account. At low enough temperature, these modes will also “freeze out”, and the specific heat decreases to zero as $T \rightarrow 0$.